

DETAILED EXPLANATION OF THE INVENTION

Industrial application field

The present invention pertains to a polyamide resin composition for under-hood parts of automobiles.

Prior art

Since polyamide 6 or polyamide 66 resin has excellent heat resistance, oil resistance, and high strength, it has recently been frequently used for parts for automobiles, and its application to functional parts such as cooling fans, radiators, tank top & bases, cylinder heads, covers, oil pans, gears, valves, and other exhaust gas system parts and fuel system parts as so-called under-hood parts or bumpers, oil caps, etc., as exterior parts has been highlighted.

However, since the polyamide 6 resin and the polyamide 66 resin essentially have a strong affinity to inorganic metal salts, molded products formed from these materials have a serious drawback in which fissure cracks are generated in a short time by the invasion of metal salts such as calcium chloride and zinc chloride. In particular, if antifreezing agent mainly composed of calcium chloride is sprayed at a large amount on a road surface to prevent the road surface freezing in the winter season attaches to under-hood parts of the automobile in a high-temperature atmosphere during traveling, fissure cracks occur in the parts and there is a risk of causing automobile trouble due to them, and additionally, causing human accidents.

On the other hand, higher polyamides such as polyamide 11 and polyamide 12 have a relatively large resistance to antifreezing agents, that is, calcium chloride and zinc chloride. Methods have been attempted that blend polyamide 6 and polyamide 66 with these higher polyamides and mold them (Japanese Kokai Patent Application Nos. Sho 57[1982]-212252, Sho 57[1982]-80448, and Sho 57[1982]-80449), as well as a method that coats molded products of polyamide 6 and polyamide 66 with thin films of higher polyamides (Japanese Kokai Patent Application No. Sho 60[1985]-155239), etc., are attempted.

Problems to be solved by the invention

The method that blends higher polyamides with polyamide 6 and polyamide 66 can obtain the calcium chloride resistance to some degree, however since they are blends, the heat resistance decrease due to the higher polyamides is large and unsatisfactory.

On the other hand, in the methods that coated thin films of higher polyamides on molded products of polyamide 6 and polyamide 66, the heat resistance, rigidity, and toughness of the surface were insufficient.

Therefore, the purpose of the present invention is to provide a polyamide resin molded product with excellent calcium chloride and heat resistance while maintaining mechanical properties of polyamide 6 or 66.

Means to solve the problems

In order to achieve the above-mentioned purpose, the present invention adopts the following means.

In other words, the polyamide resin composition of the present invention is characterized by the fact that a molded product composed of polyamide 6 and/or polyamide 66 is coated with a thin film with a thickness of 10-750 μ composed of a mixture of 85-50 wt% polyamide 6 and/or polyamide 66 and 15-50 wt% polyolefin group ionomer resin.

The polyamide 6 and/or the polyamide 66 being used in the present invention mean a homogeneous polymerized product composed of polyamide 6 or polyamide 66, a copolymerized product of polyamide 6 and polyamide 66, or a blend of them. In this sense, a term of “and/or” and a symbol are used. Furthermore, other polyamide components may also be copolymerized or blended at a small amount in the range where the properties of polyamide 6 and polyamide 66 are not considerably damaged.

Next, a polyamide molded product is obtained. The molded product is obtained by well-known methods, that is, the injection molding method, extrusion method, or blow molding method. During molding, if necessary, glass fibers, carbon fibers, other inorganic fillers such as wollastonite, talc, and clay, glass beads, and organic fibers can be mixed at 0-60 wt%.

On the other hand, a modified polyamide resin for coating on the polyamide molded product is prepared. This resin is a blended modified nylon 6 and/or blended modified nylon 66 constituted by mixing 85-50 wt% polyamide 6 and/or polyamide 66 and 15-50 wt% olefin group ionomer resin. The olefin group ionomer is a resin in which a copolymer of olefins such as ethylene and propylene and an unsaturated carboxylic acid such as acrylic acid and methacrylic acid is partially or entirely neutralized with a metal, and industrial products on the market such as “Sarin [transliteration],” “Himiran [transliteration],” and “Koporen [transliteration]” can be used.

In the manufacture of the polyamide resin composition of the present invention, there is (a) a method that prepares a film composed of an olefin group ionomer modified polyamide, pastes the film on a mold, and forms a film on the surface of a molded product by molding

polyamide 6 and/or polyamide 66, or (b) a method that fixes a polyamide molded product molded in advance into a mold, and forms a film by injection-molding an olefin group ionomer modified polyamide on the surface of the molded product, or (c) a method that forms an olefin group ionomer modified polyamide film by a hot press, or (d) a method that prepares a molded product having the same shape as that of an intended molded product by a thin film composed of an olefin group ionomer modified polyamide, fixes it into a mold, and molds the polyamide resin, or (e) a method that forms a film by a so-called two-color molding for simultaneously injection-molding polyamide 6 and/or polyamide 66 resins and an olefin group ionomer modified polyamide from each cylinder by using an injection molding machine having two cylinders. Especially, the methods (a), (b), and (e) are preferable.

The thickness of the film is 10-750 μ , preferably 20-450 μ . If the thickness is smaller than 10 μ , the film manufactured in advance by the method that forms a thin film is broken by the molding pressure during molding or is not fluidized by an injection molding in the injection molding method, a film cannot be formed on the entire surface of a polyamide molded product.

If the thickness is greater than 750 μ , since the ratio of the film to the weight of the polyamide resin molded product being coated is increased, excellent heat resistance and rigidity of the molded product are lowered, which is not preferable.

In the polyamide resin molded product obtained in this manner, since the film formed on the surface is very thin, the metal chloride resistance is very distinctly improved without damaging the characteristics of the molded product composed of polyamide 6 and polyamide 66 resins, and no fissure cracks are generated. Also, since the weight of the thin film required for coating of the molded product is slight, the cost is low. Furthermore, since it is not a so-called coated film, pinholes are not generated.

Application examples

Next, application examples of the present invention are mentioned in detail.

Also, the method for evaluating the calcium chloride resistance of molded products obtained by the application examples and the comparative examples was as follows.

The molded products are conditioned in advance for 40 h in hot water at 100°C, and 5% CaCl_2 solution was dropped on the surface of 0.5 cc molded product, and held for 2 h in a gear oven at 100°C.

After repeating 10 cycles of said treatment (conditioning \rightarrow CaCl_2 solution drop \rightarrow holding in the oven), the existence of cracks on the molded product surface was enlarged 30 times by an optical microscope and confirmed.

Application Example 1

A film with a thickness of 100 μ of a blended modified nylon 6 obtained by melting and mixing 40 wt% Zn^{2+} type ethylene group ionomer "Himiran [transliteration] 1855 (made by Mitsui Polychemical K.K.) with nylon 6 was prepared, and said film was pasted to the fixed side of a mold for a small-scale wheel cap molded product (a plate-shaped molded product with a diameter of 100 mm and a thickness of 3 mm) for automobiles mounted in an injection molding machine, Meiki SJ-35B (made by Meiki Seisakusho K.K.). In a state in which the film was pasted, the mold was warmed to 80°C, and the mold was closed. Then, a polyamide 66 reinforced with 30% glass fibers ("CM3001G-30" made by Toray Industries, Inc.) was molded under the conditions of a cylinder temperature of 280°C, an injection pressure of 450 kg/cm², and a molding cycle injection of 10 sec/cooling of 12 sec.

A molded product that had no film fracture and had uniform appearance and good film adhesion was obtained.

The calcium chloride resistance of the molded product obtained in this manner was investigated by the above-mentioned method. As a result, no cracks were generated at all, even by 10 cycles of treatment, and the calcium chloride resistance was very good.

Comparative Example 1

A small-scale wheel cap molded product (a plate-shaped molded product with a diameter of 100 mm and a thickness of 3 mm) of only "CM3001G-30" (without a film) of Application Example 1 was obtained under the same molding conditions, using the same mold as that used in Application Example 1. The calcium chloride resistance of said molded product was evaluated. As a result, cracks with a depth of about 0.2 mm were generated on the entire surface on which an aqueous calcium chloride solution was dropped by only one cycle of the treatment.

Application Example 2

A film with a thickness of 50 μ of a blended modified nylon 66 obtained by melting and mixing 40 wt% olefin group ionomer "Koporen 7800" (made by Dow-Asahi K.K.) with nylon 66 was prepared, and said film was pasted to the fixed side of a mold for a box type molded product (50 mm in width x 80 mm in length x 20 mm in height, 2.5 mm in thickness) mounted in an injection molding machine, Meiki SJ-35B. Similarly to Application Example 1, the mold was conditioned (80°C), and using a reinforced polyamide 66 resin ("CM3001N" made by Toray Industries, Inc.), a box type molded product coated with a modified polyamide 66 film was

obtained by injection-molding under the conditions of a cylinder temperature of 280°C, an injection pressure of 400 kg/cm², a molding cycle injection of 12 sec, and a cooling cycle of 15 sec.

The obtained molded product had no film fracture and had uniform appearance and good film adhesion was obtained.

The calcium chloride resistance of the molded product obtained in this manner was investigated by the above-mentioned method. As a result, no cracks were generated at all in the molded product, even by 10 cycles of the treatment.

Comparative Example 2

Using the same mold as that of Application Example 2, under the same molding conditions, a box type molded product was obtained only by "CM3001N" without pasting a modified polyamide 66 film. The calcium chloride resistance of said box type molded product was evaluated. As a result, large cracks with a depth of about 1.5 mm were generated by only one cycle.

Application Example 3

A film with a thickness of 150 μ of the same blended modified nylon 6 as that used in Application Example 1 was used, and a non-reinforced polyamide 6 resin ("CM1017" made by Toray Industries, Inc.) was employed as a material to be injection-molded. A small-scale wheel cap molded product having uniform appearance and good film adhesion coated with a modified nylon 6 film was obtained by the same method as that of Application Example 1.

An aqueous calcium chloride solution was dropped on the surface coated with the film, and the calcium chloride resistance was investigated. As a result, no cracks were generated at all in the molded product, even by 10 cycles of the treatment.

Comparative Example 3

Using the same mold as that of Application Example 3, under similar molding conditions, a small-scale wheel cap molded product was obtained only by injection-molding only "CM1017N" without pasting a film.

The calcium chloride resistance of said molded product was investigated. As a result, large cracks with a depth of about 1.6 mm were generated on the entire surface of the dropped part of the aqueous calcium chloride solution by only one cycle of the treatment.

Application Example 4

Using Meiki SJ-35B injection molding machine, a disk molded product with a diameter of 50 mm and a thickness of 4.0 mm was obtained by injection-molding a polyamide 6 resin reinforced with 30% glass fibers ("CM1011G-30" made by Toray Industries, Inc.) under the conditions of a cylinder temperature of 265°C, a mold temperature of 90°C, an injection pressure of 350 kg/cm², a molding cycle of 10 sec and a cooling cycle of 10 sec. Said molded product was fixed into a cavity carved into a disk shape of a diameter of 50.1 mm and a thickness of 4.4 mm, and the mold was conditioned to 90°C. Then, the same blended modified nylon 6 resin as that used in Application Example 1 was injection-molded under the conditions of a cylinder temperature of 275°C, an injection cycle of 10 sec, and a cooling cycle of 10 sec using a film gate with 0.8 mm thickness, 15 mm width, and 2 mm length.

The molded product obtained was a molded product in which the disk molded product surface with a thickness of 4.0 mm of "CM1011G-30" was coated with a blended modified nylon 6 resin with a thickness of 420 μ .

An aqueous calcium chloride solution was dropped on the surface coated with the blended modified nylon 6, and the calcium chloride resistance of said molded product was investigated. As a result, no cracks were generated at all in the molded product, even by 10 cycles of the treatment.

Effects of the invention

In the polyamide resin molded product of the present invention, since the molded products of polyamides 6 and 66 are coated with thin films of ionomer blended modified polyamides 6 and 66, the excellent properties of the polyamides 6 and 66 are maintained as they are, the surface has the calcium chloride resistance, and the generation of cracks is prevented.

Therefore, the present invention is useful especially in under-hood parts such as radiator tanks of automobiles.

Language Services Unit
Phoenix Translations Services
June 9, 2006